



LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

Extreme thermodynamic conditions: novel stoichiometries, violations of textbook chemistry, and intriguing possibilities for the synthesis of new materials.

E. Stavrou

March 8, 2016

APS March Meeting
Baltimore, MD, United States
March 14, 2016 through March 18, 2016

Disclaimer

This document was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor Lawrence Livermore National Security, LLC, nor any of their employees makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or Lawrence Livermore National Security, LLC. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or Lawrence Livermore National Security, LLC, and shall not be used for advertising or product endorsement purposes.

Extreme thermodynamic conditions: novel stoichiometries, violations of textbook chemistry, and intriguing possibilities for the synthesis of new materials.

Elissaios Stavrou

The logo for Lawrence Livermore National Laboratory, consisting of a stylized "U" and "L" shape.

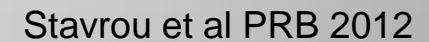
**Lawrence Livermore
National Laboratory**

LLNL-PRES-

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. Lawrence Livermore National Security, LLC

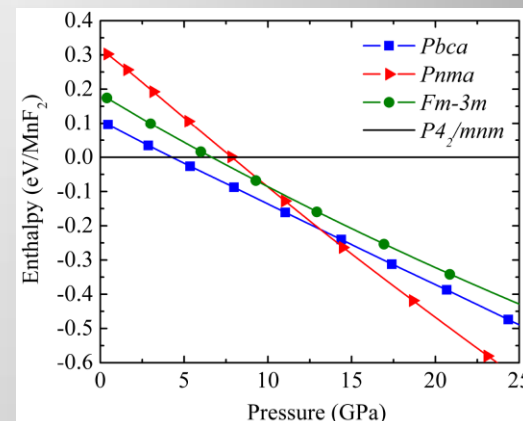
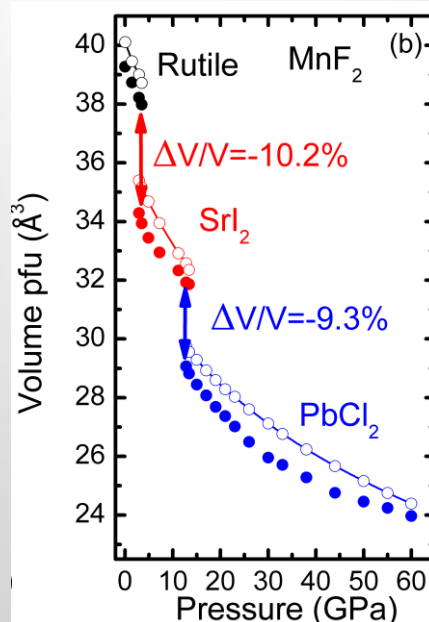
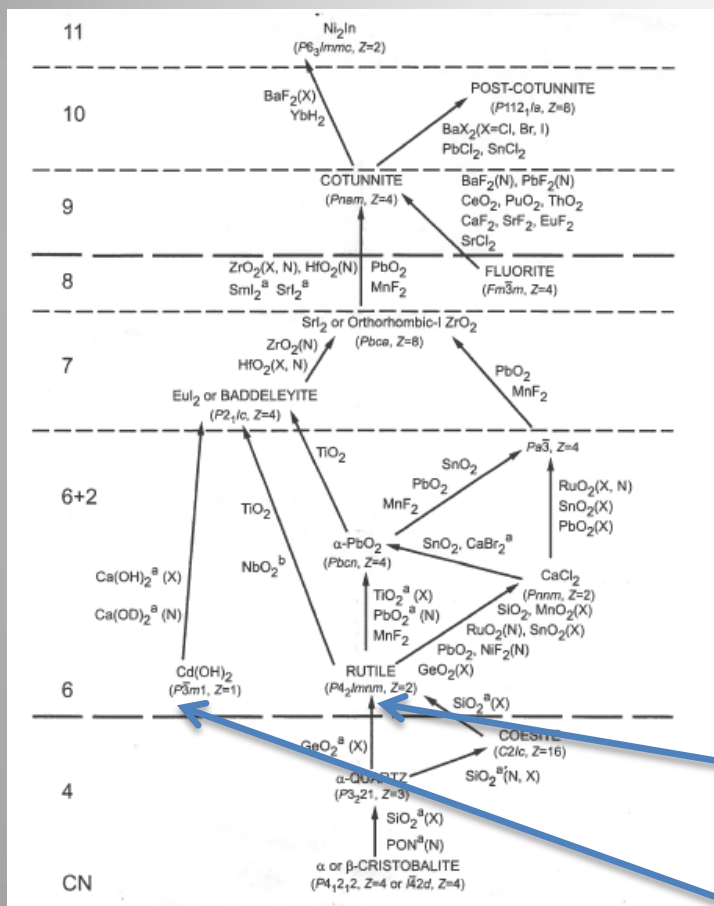


NE rule of Bastide's diagram



Materials in Extremes: High-pressure Synthesis of New Materials.

(Materials in Extremes: Bridging Simulation and Experiment.)



Stavrou et al. 2016



Courtesy K. Syassen

Of course things are not always that easy: MgCl_2

Materials in Extremes: High-pressure Synthesis of New Materials.



Stoichiometry: unknown,
Structure: unknown,
Stability: unknown

Black cat analogy

Philosophy is like being in a dark room and looking for a black cat.

Metaphysics is like being in a dark room and looking for a black cat that isn't there.

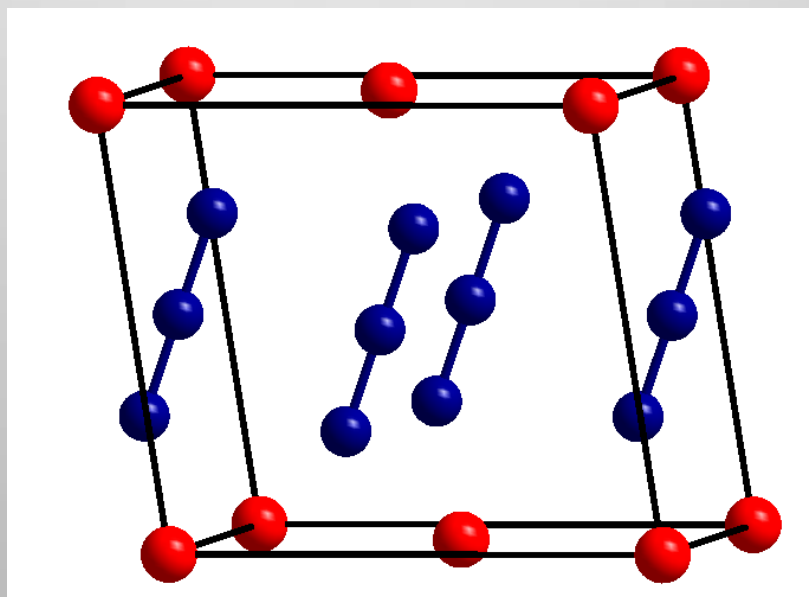
High-pressure Synthesis of New Materials is like being in a dark room and looking

for a
Pink Horse
Green Dog
Blue Cat
Black Flamingo
that some times is there.

Nitrogen again.....

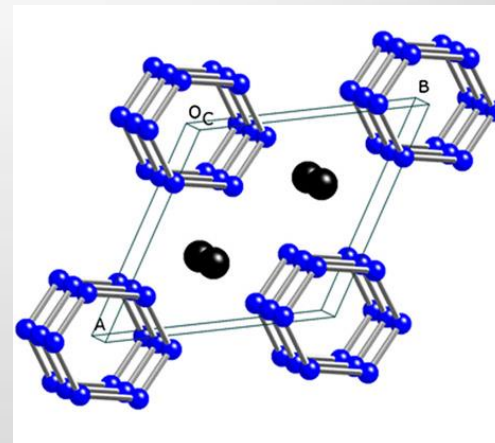
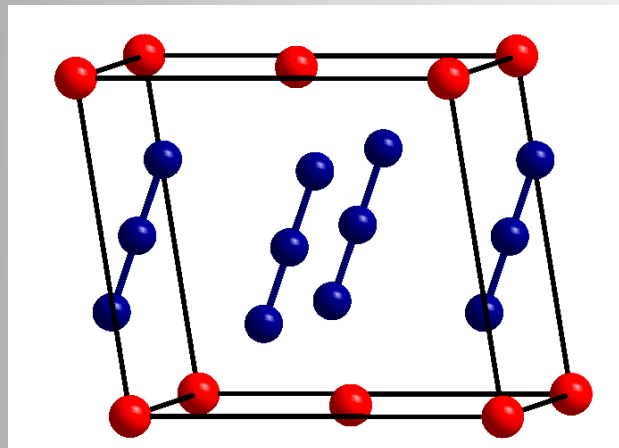
Is it possible to form nitrogen rich compounds?
Without need of extreme thermodynamic conditions and (meta)stable at ambient conditions?

Azides: a >10y old story, use of N_3 linear anions to form high nitrogen entities.



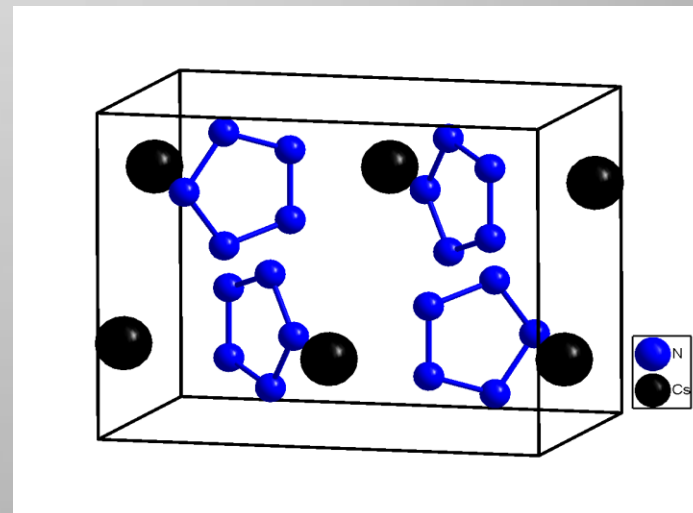
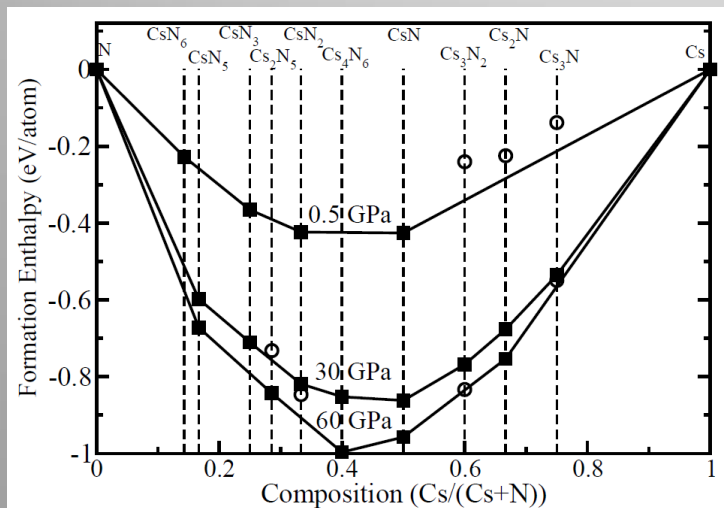
Alkali metal azides (AN₃)

Prediction of N₆ rings formation under pressure starting from alkali metal azides
However, the relative stoichiometry remains the same: 1/3

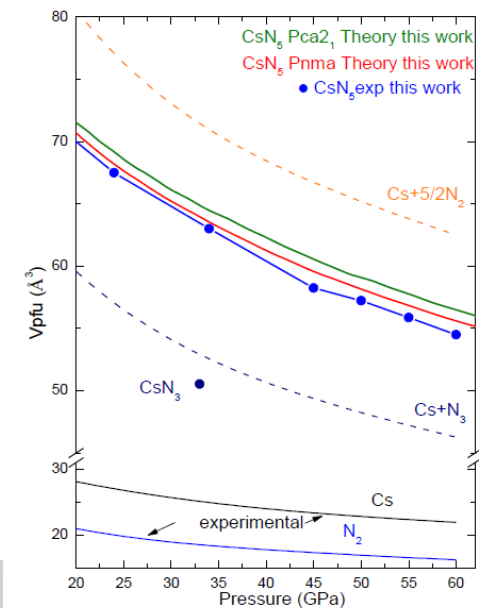
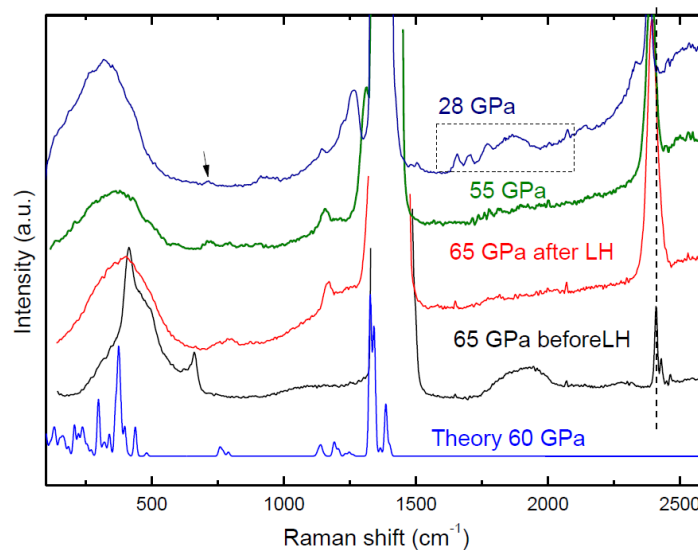
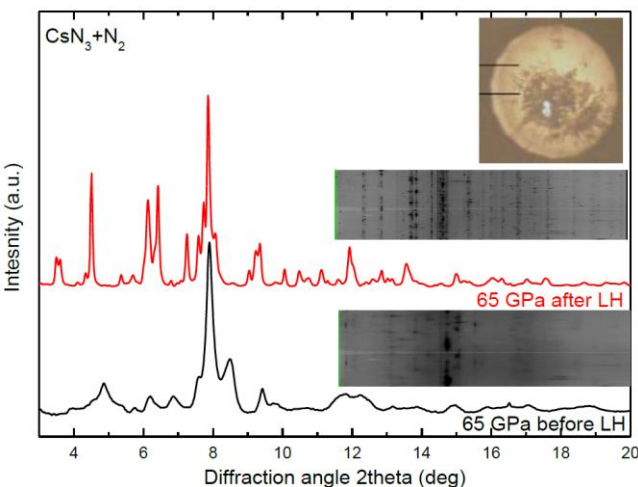


e.g. Jie Zhang 2014

Search of the most stable stoichiometry under pressure



Experimental observation of CsN_5 compound



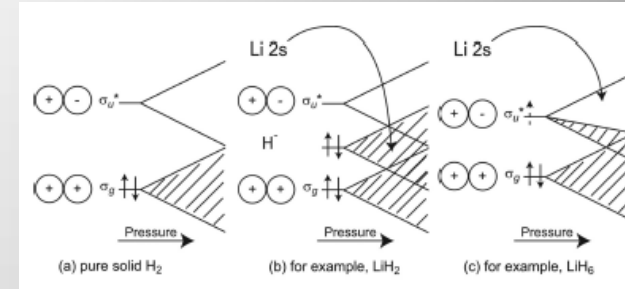
- Synthesis of a wide band gap compound at 60 GPa above 2000K
- Both Raman and XRD measurement suggest the formation of CsN_5
- The synthesized compound remains stable up to 18 GPa

Steele *et al.* in preparation

Pure Hydrogen vs Metal polyhydrides

H-Metallic and superconducting at pressures >450 GPa with T_c up to 240 K.

- Impurity (e.g.) metal promote metallization and T_c at lower pressure:
- 'chemical pressure' increases the electronic DOS
- electronic level hybridization with
- a consequent electron transfer and metallization.

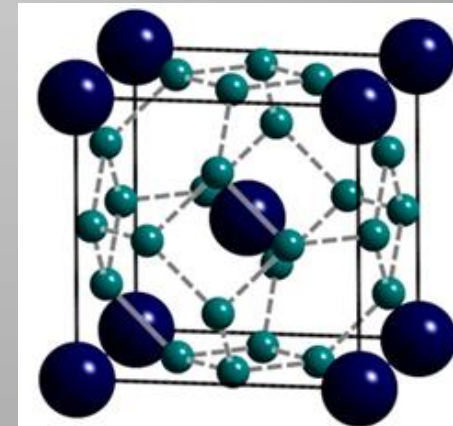
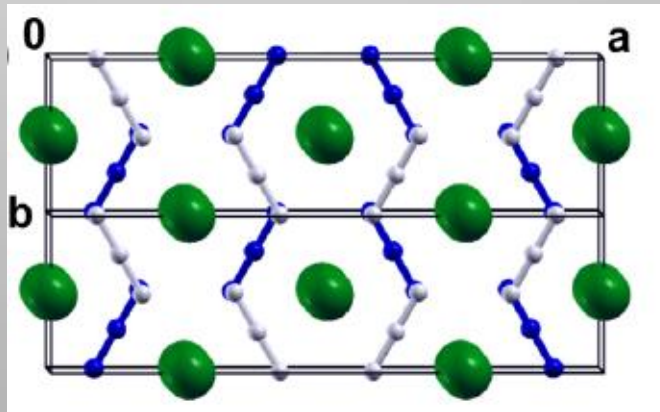
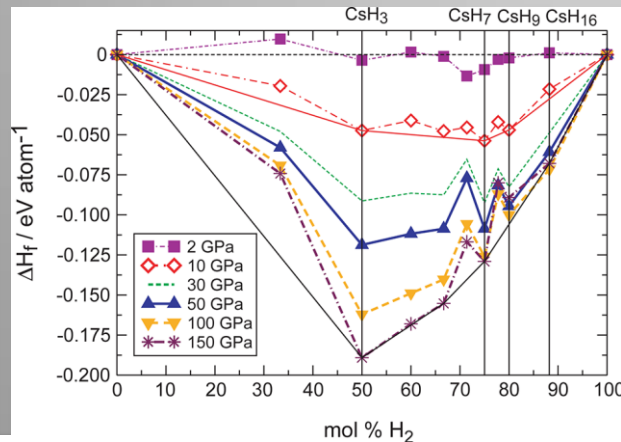


MPH have very high hydrogen density, higher than liquid or solid hydrogen.

Recent theoretical studies: alkali AH_n (with $n > 1$) and alkaline earth ($n > 2$) MPH at pressures as low as a few (<10) GPa.

CsH_3 is expected to become metallic at about 50 GPa.

CaH_6 is expected to be stable under pressure with a T_c of >220 K at 150 GPa.



Conventional superconductivity at 203 kelvin (P=90 GPa)

NATURE | LETTER

日本語要約

Conventional superconductivity at 203 kelvin at high pressures in the sulfur hydride system

A. P. Drozdov, M. I. Eremets, I. A. Troyan, V. Ksenofontov & S. I. Shylin

[Affiliations](#) | [Contributions](#) | [Corresponding author](#)

Nature **525**, 73–76 (03 September 2015) | doi:10.1038/nature14964

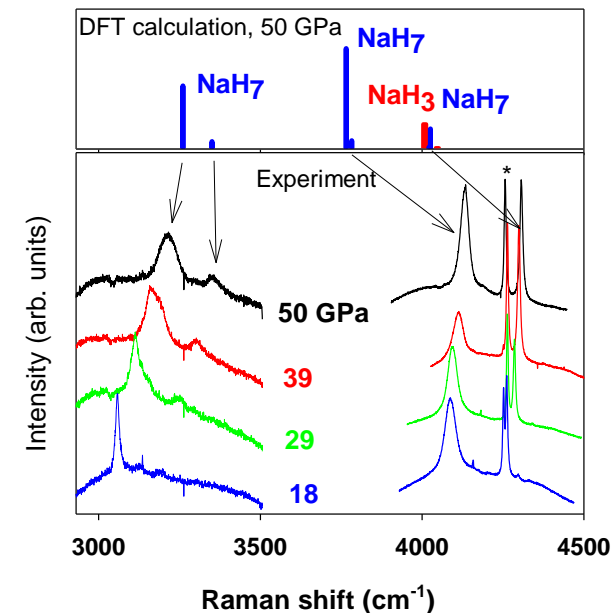
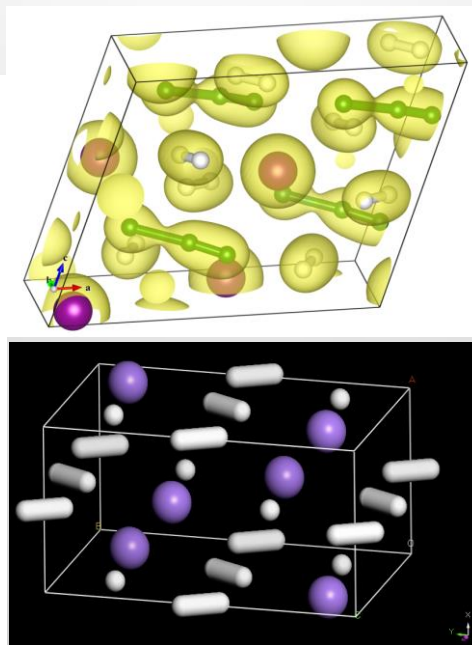
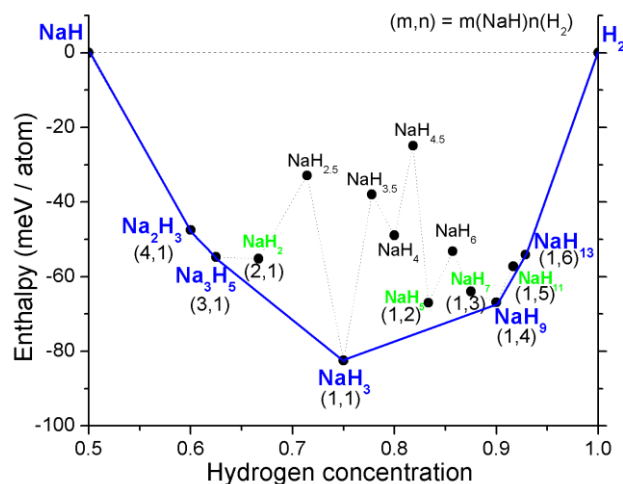
Received 25 June 2015 | Accepted 22 July 2015 | Published online 17 August 2015

BCS-like superconductivity

Stoichiometry: unknown
Structure: unknown

Sodium polyhydrides

In spite of several theoretical predictions, extensive experimental searches for MPH remain unsuccessful

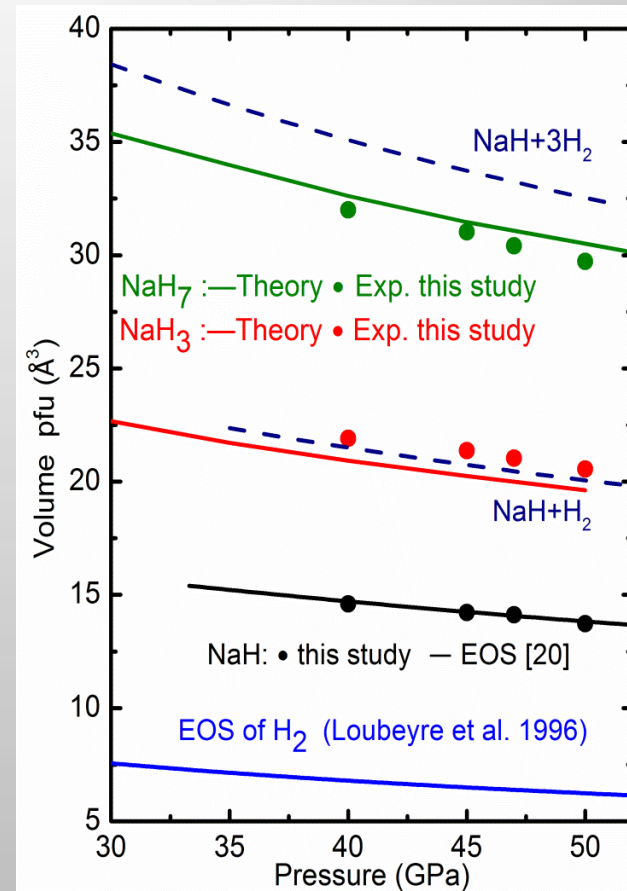
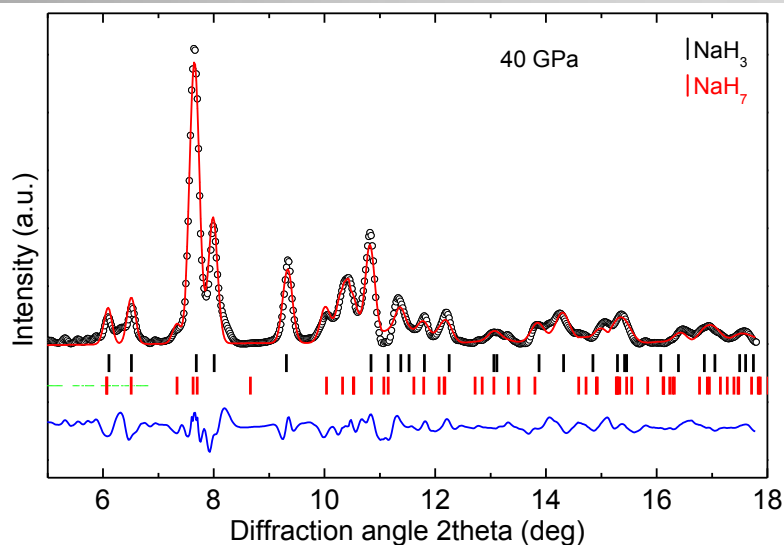
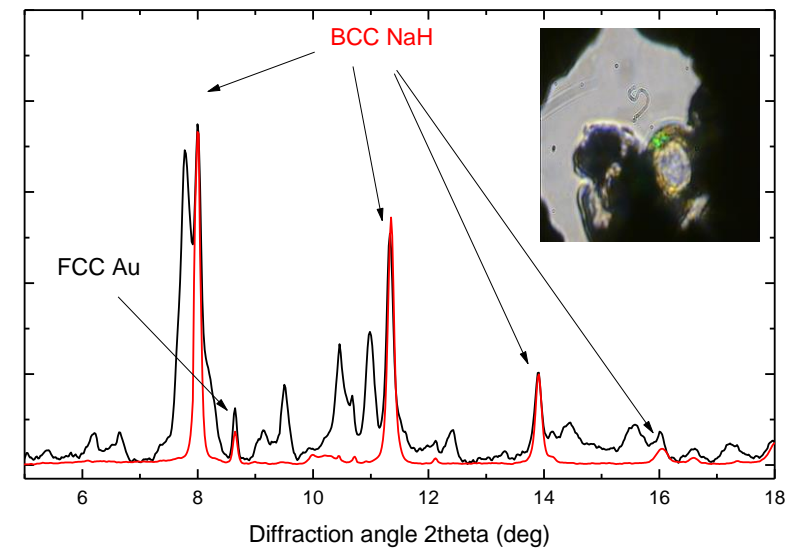


Experimental synthesis of NaH₇ and NaH₃ starting from NaH at ca 50 GPa
Formation of H₃ linear anions

Struzhkin et al. Nat. comm. accepted

Sodium polyhydrides

In both Raman and XRD measurements a mixture of NaH_3 and NaH_7 is observed



Consider the *xenon paradox*:*

In the atmospheres of Earth and Mars, xenon is strongly depleted relative to argon, when compared to the abundances in chondritic meteorites

Where is the missing xenon?

*to not be confused with **Zeno's paradoxes**, a set of philosophical problems generally thought to have been devised by philosopher Zeno of Elea (ca. 490–430 BC) to support that motion is nothing but an illusion.



Where the xenon went? missing xenon paradox

First Scenario: Disappeared from early earth.

LETTER

doi:10.1038/nature11506

The origin of the terrestrial noble-gas signature

Svyatoslav S. Shcheka¹ & Hans Keppler¹

Second scenario: Trapped inside Ag zeolites

nature
chemistry

ARTICLES

PUBLISHED ONLINE: 20 JULY 2014 | DOI: 10.1038/NCHEM.1997

Irreversible xenon insertion into a small-pore zeolite at moderate pressures and temperatures

Donghoon Seoung¹, Yongmoon Lee¹, Hyunchae Cynn², Changyong Park³, Kwang-Yong Choi⁴, Douglas A. Blom⁵, William J. Evans², Chi-Chang Kao⁶, Thomas Vogt⁵ and Yongjae Lee^{1*}

Where the xenon went? missing xenon paradox

Third Scenario: Bonded with Fe/Ni in Earth's core

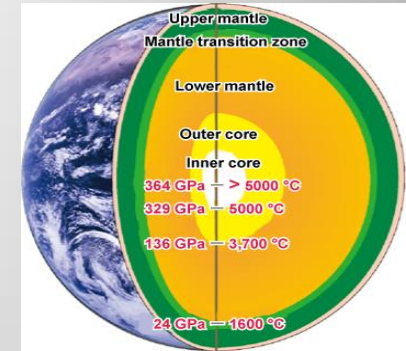


GEOPHYSICAL RESEARCH LETTERS, VOL. 37, L04302, doi:10.1029/2009GL041953, 2010

No reactions observed in Xe-Fe system even at Earth core pressures

D. Nishio-Hamane,¹ T. Yagi,¹ N. Sata,² T. Fujita,^{1,3} and T. Okada¹

Received 27 November 2009; revised 12 January 2010; accepted 21 January 2010; published 20 February 2010.



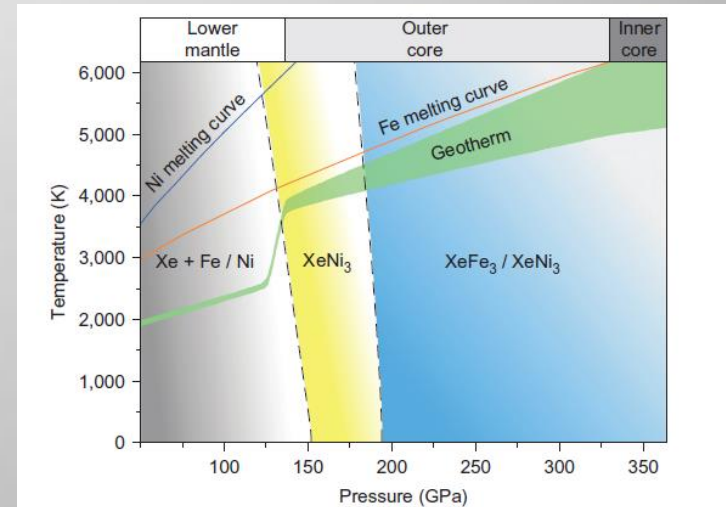
ARTICLES

PUBLISHED ONLINE: 20 APRIL 2014 | DOI: 10.1038/NCHEM.1925

nature
chemistry

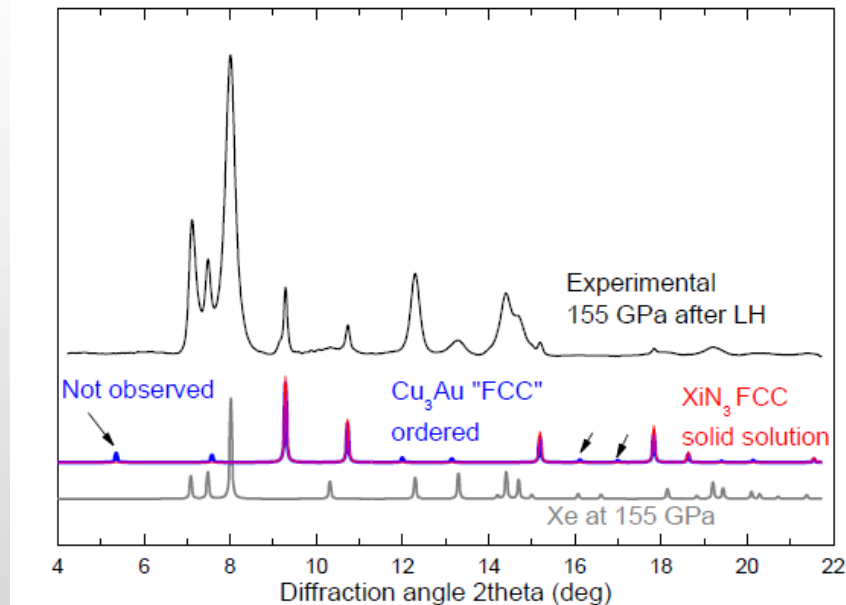
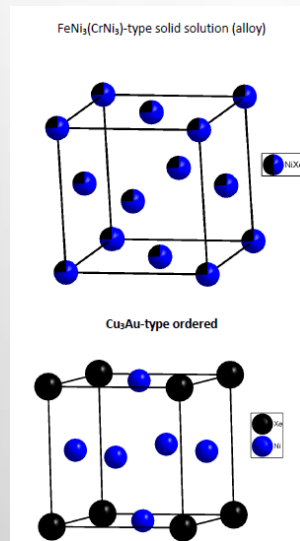
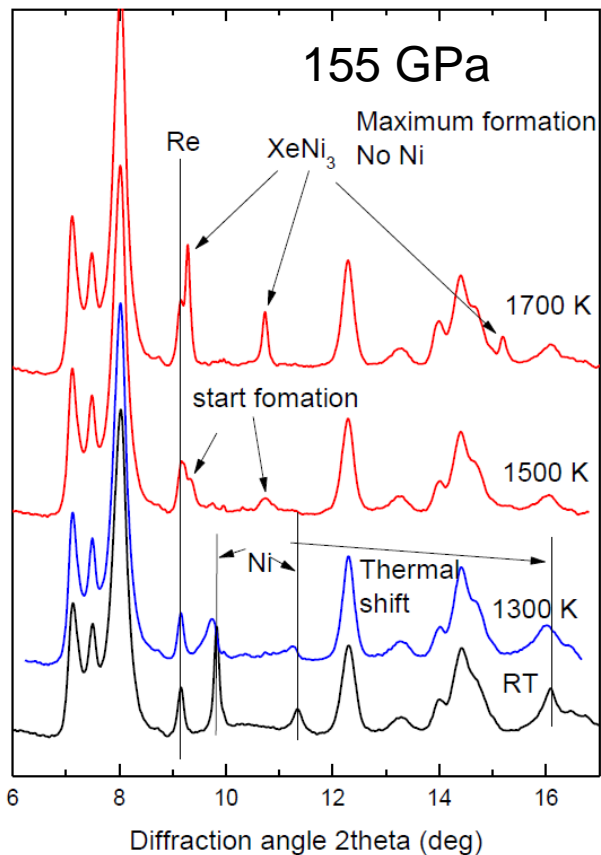
Reactions of xenon with iron and nickel are predicted in the Earth's inner core

Li Zhu¹, Hanyu Liu¹, Chris J. Pickard², Guangtian Zou¹ and Yanming Ma^{1*}



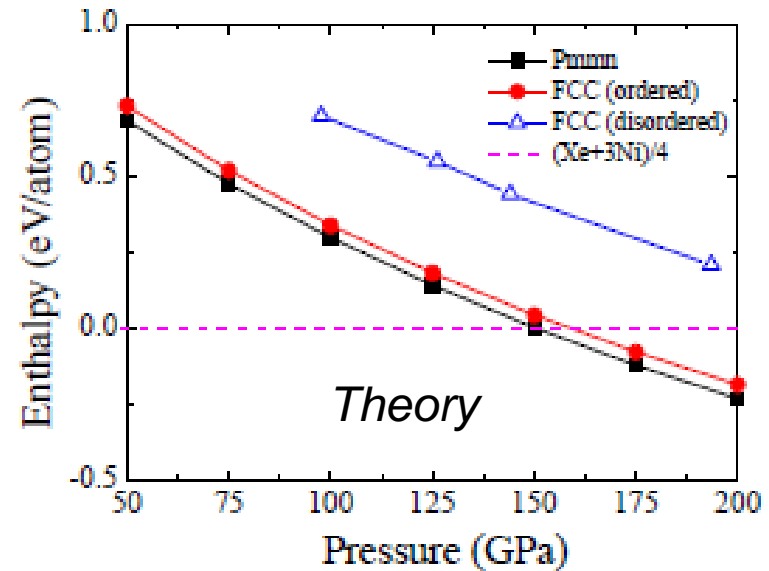
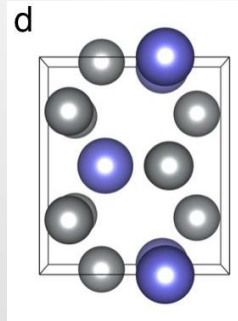
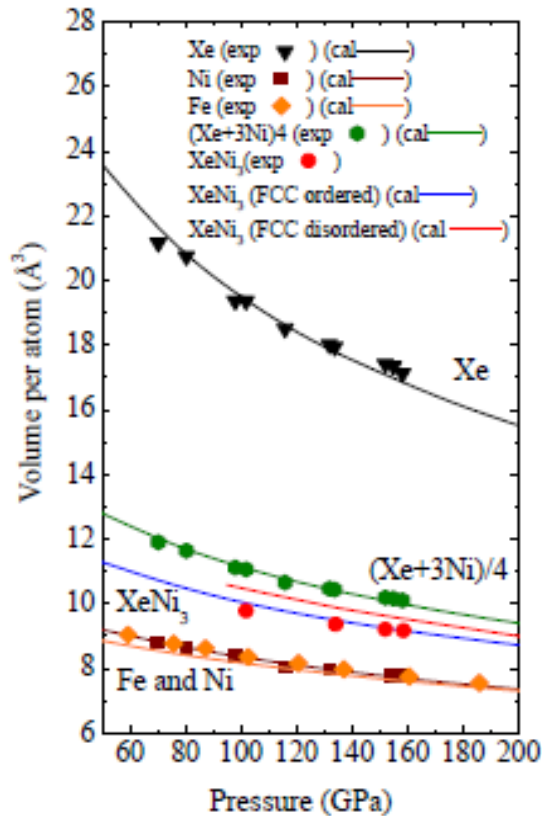
Prediction of XeNi₃ and XeFe₃ compounds stable under core conditions.
What about an Fe/Ni alloys?
Earth core: Fe + Ni(5-10%)

I. Ni-Xe mixture – formation of XeNi_3 compound



- Formation of a solid solution FCC Ni/Xe compound at 155 GPa and $>1500\text{K}$
- Cell volume suggests a XeNi_3 stoichiometry

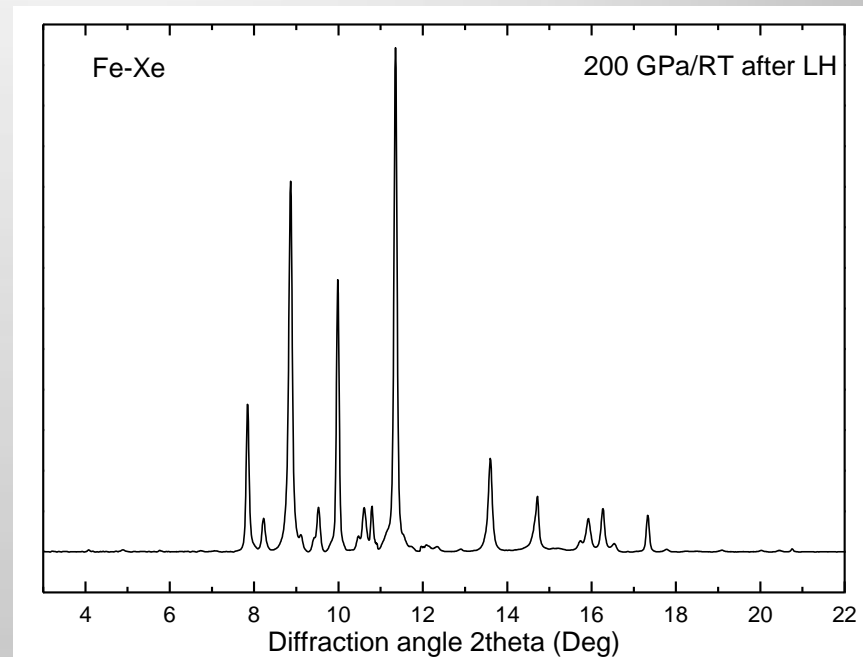
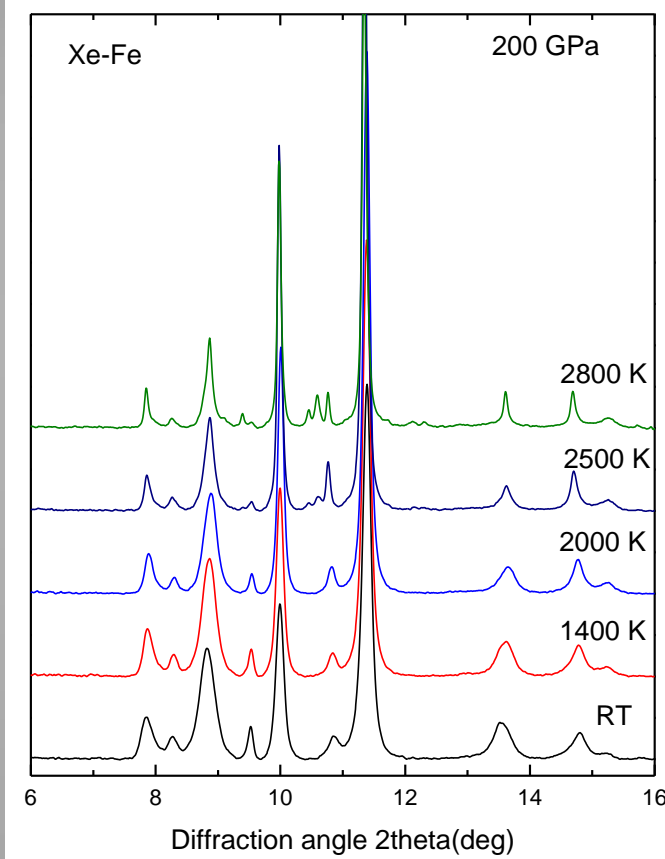
I. Ni-Xe mixture – formation of XeNi_3 intermetallic alloy



- XeNi_3 is ca 10% denser than the Xe-Ni superposition, implying strong bonding between Xe-Ni
- The FCC structure is competitive with the predicted Pmmn XeNi_3

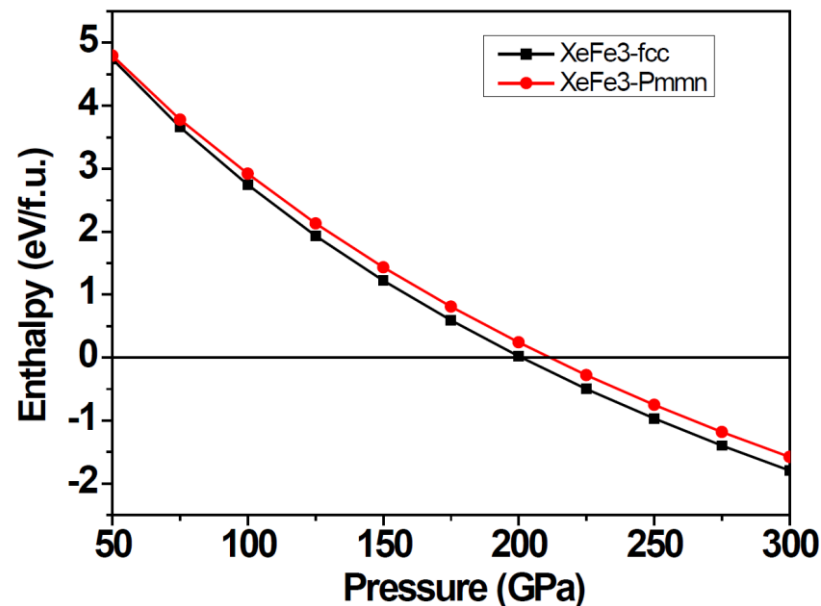
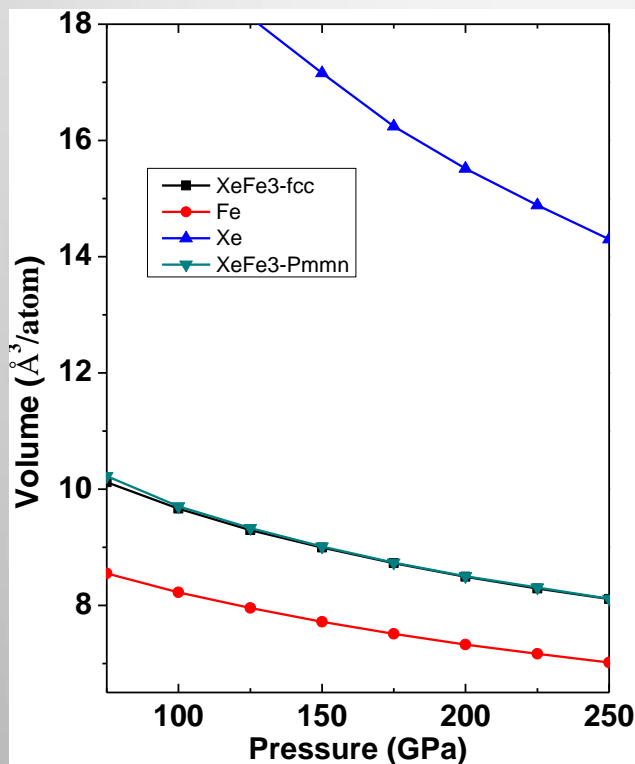
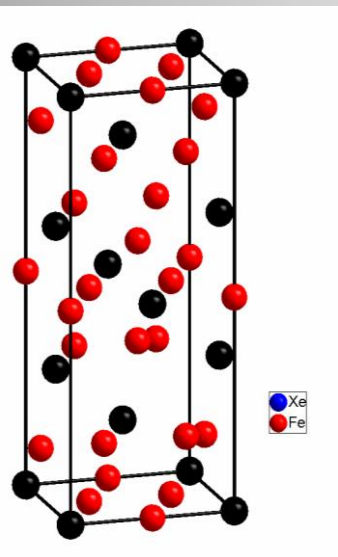
II. Fe-Xe mixture – formation of XeFe_3 compound

- 200 GPa and 2000 K threshold for synthesis
- The synthesized compound is quenchable to RT



II. Fe-Xe mixture – formation of XeFe_3 compound

- We tentatively adopt a NbPd_3 -type structure
- The Pmmn structure is competitive with the predicted FCC XeFe_3



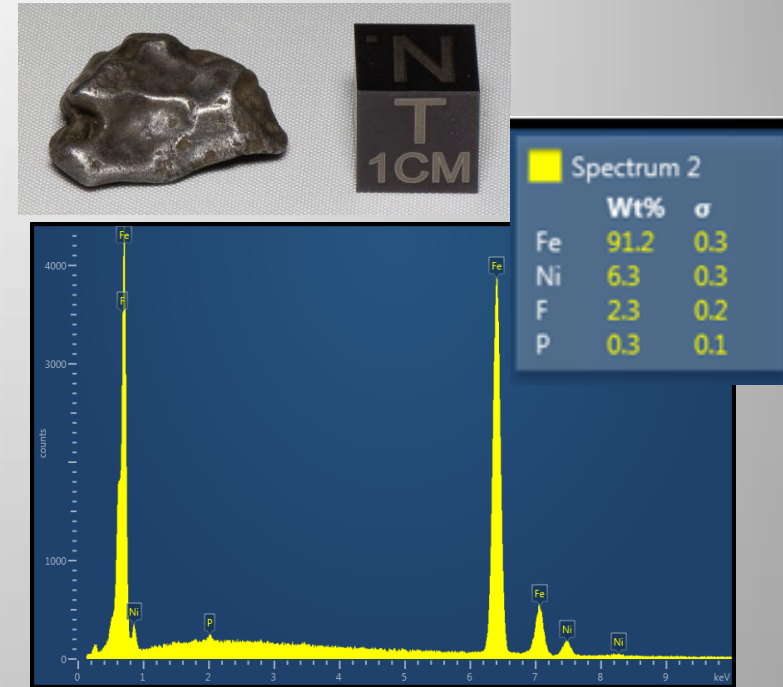
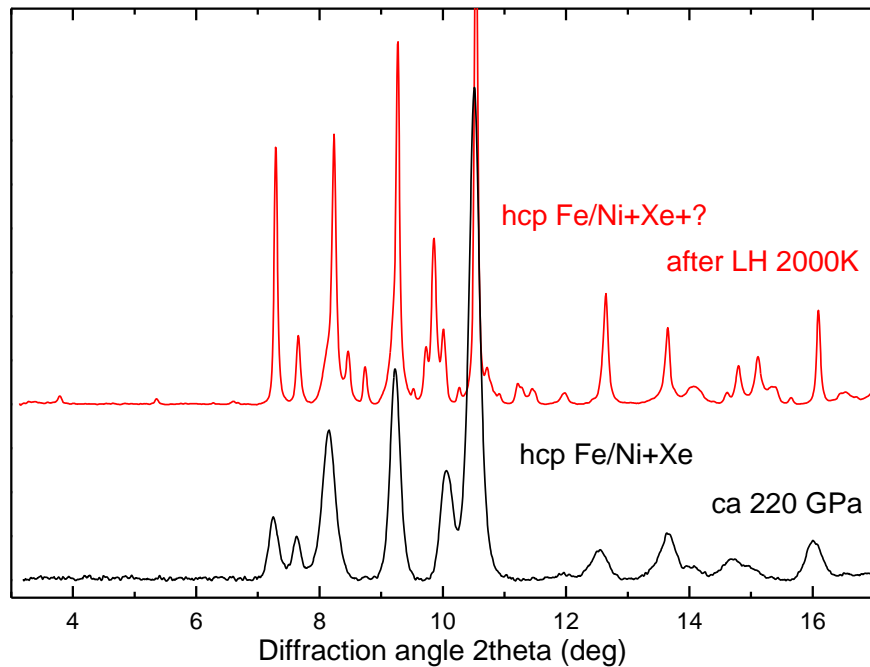
III. Real core: Fe/Ni alloy-formation of $\text{Xe}(\text{Fe}/\text{Ni})_3$ compound

“The missing Fe/Ni alloy paradox”

Fe/Ni alloy (5-10% Ni) was difficult to obtain commercially.

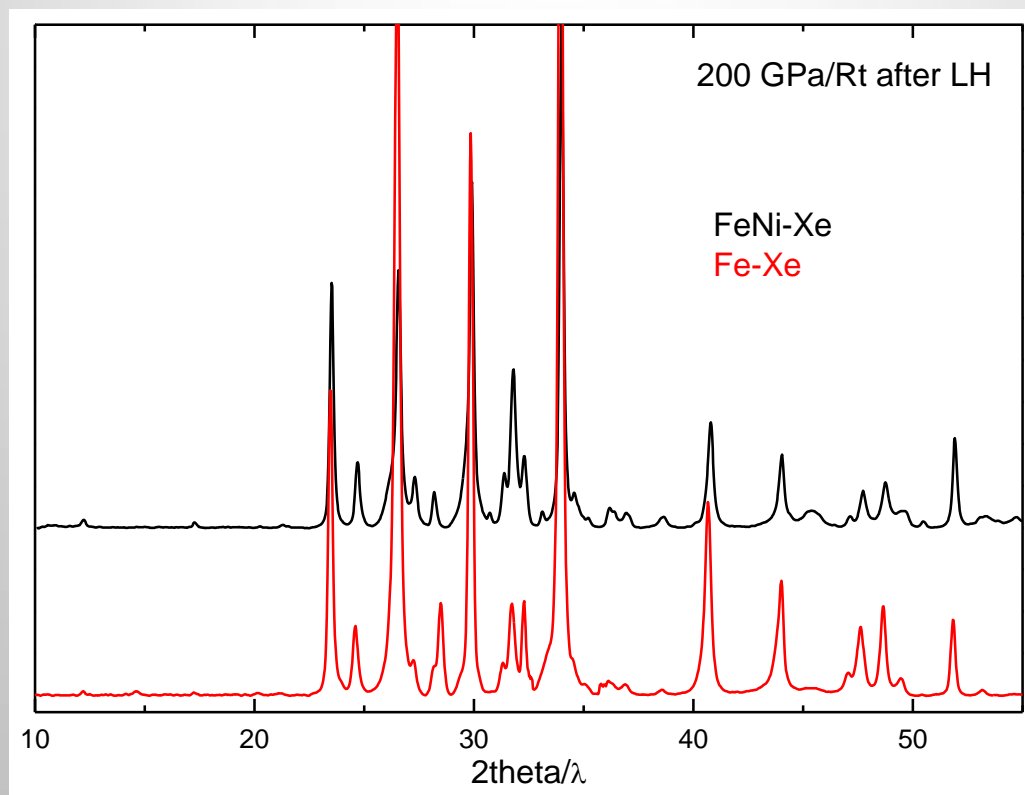
Sikhote-Alin Meteorite

So, we have used a “real piece”!



Formation of a $\text{Xe}(\text{Fe}/\text{Ni})_3$ compound, tentatively characterized as an orthorhombic NbPd_3 -type solid solution (Fe/Ni)

Comparison between starting mixtures: Xe-Fe vs Xe-(Fe_{0.93}Ni_{0.07})



- Identical patterns of the synthesized compounds-
- Fe/Ni remain in a SS arrangement in Xe(Fe_{0.93}Ni_{0.07})₃

More paradoxes

If Xe is present in Earth core then what about the “low density anomaly”?
Our planet’s core has lower density than a Fe/Ni alloy This could be explained
by the presence of lighter elements e.g. hydrogen and carbon

Birch 1952

**Unwary readers should take warning that ordinary language undergoes modification to a high-pressure form when applied to the interior of the Earth; a few examples of equivalents follow:*

High-pressure form:

certain
undoubtedly
positive proof
unanswerable argument
pure iron

Ordinary meaning:

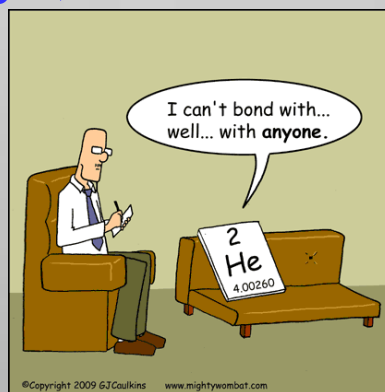
dubious
perhaps
vague suggestion
trivial objection
uncertain mixture of all the
elements

Compounds with Xe and electronegative elements are known (Xe-Cl and Xe-O)

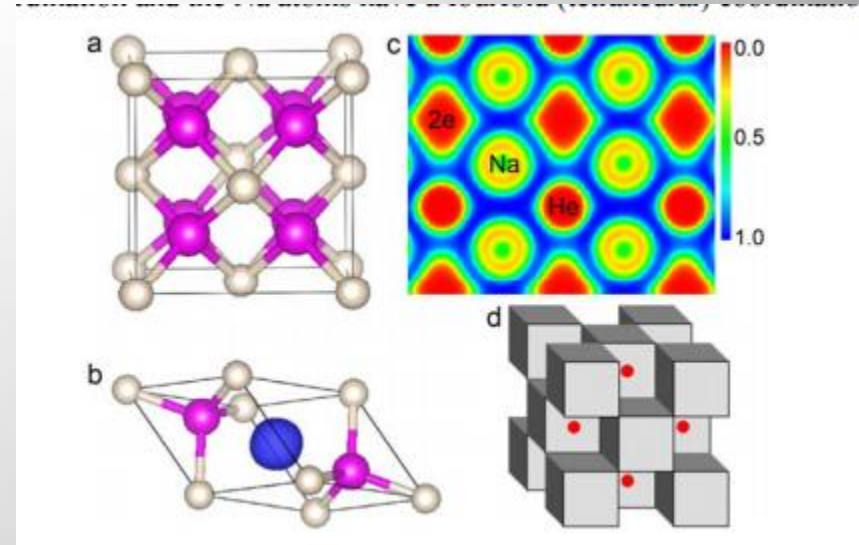
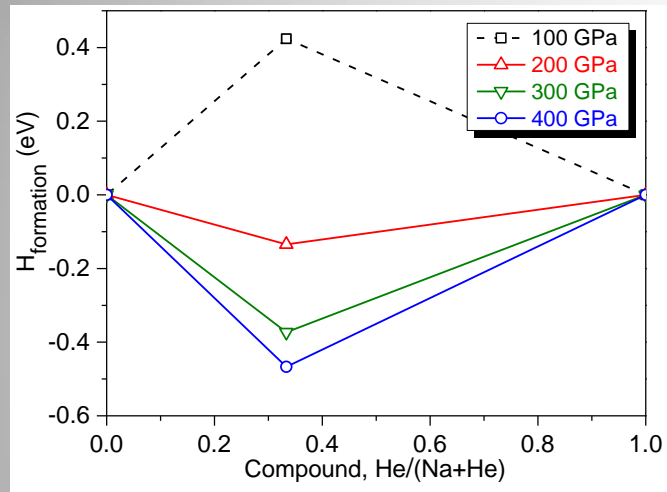
In the case of Xe-Ni/Fe compounds:

i) Fe is an oxidant rather than a reductant ? ii) Xe is negatively charged?

Of course Xe is ‘on the edge’, but what exactly noble gas means?



Stable Compound of Helium and Sodium at High Pressure

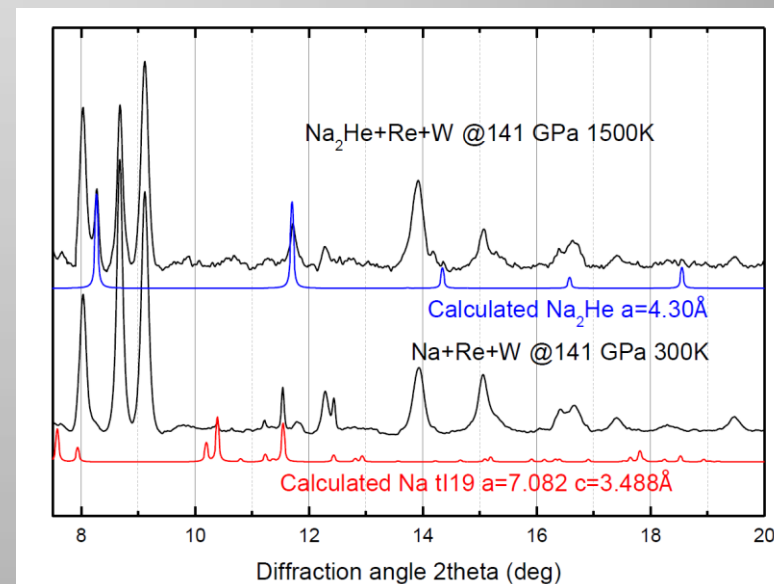
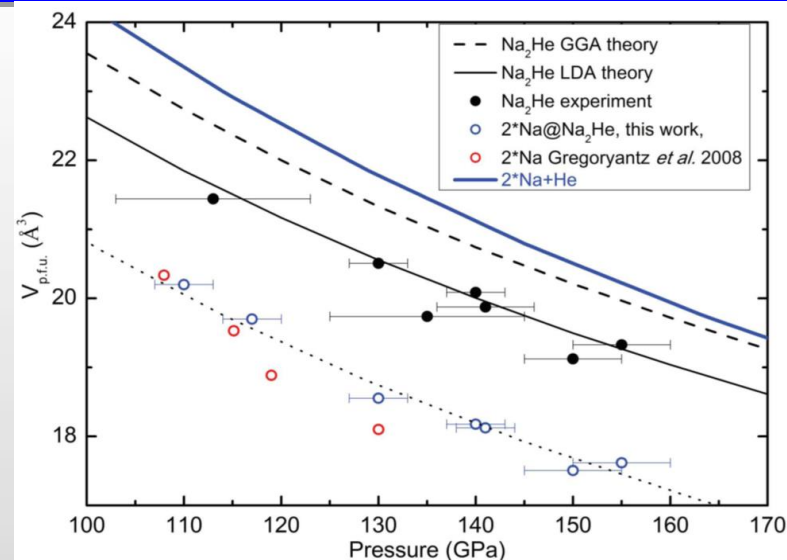
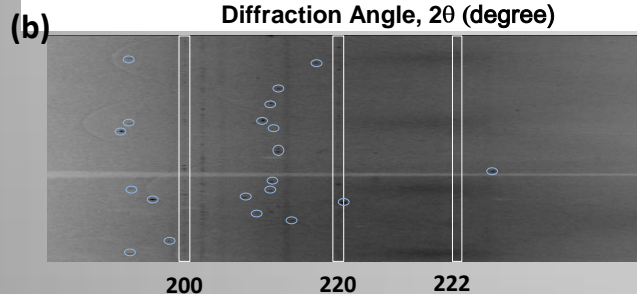
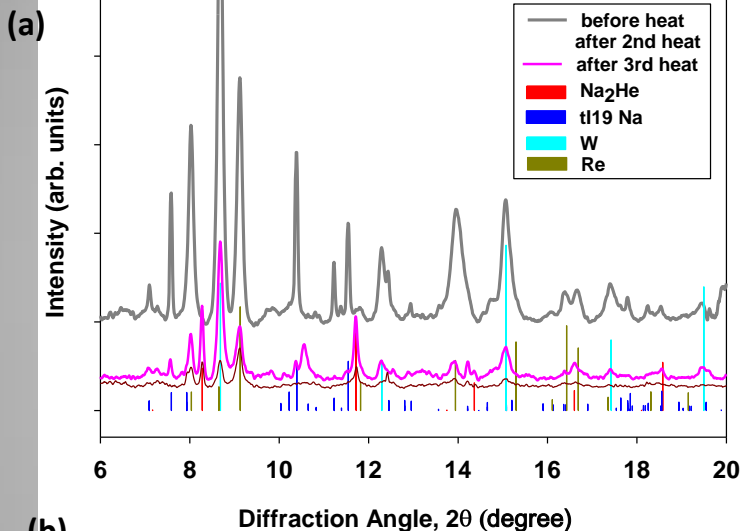


CaF₂-like Na₂He multi center-electride structure

Does this really exist?
Is it a real bonding?

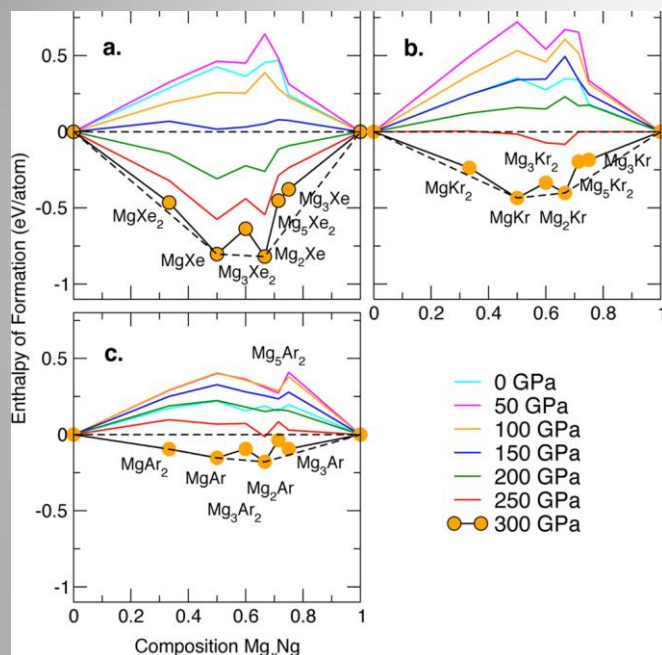
Dong et al. under review 2016

Experimental observation of Na₂He



We observe a 5% volume reduction in comparison to superposition of 2Na+He
Na₂He remains stable at HT \gg Na melting.

Reactivity of NG under extreme conditions, Mg-NG case study



J | A | C | S
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Article
pubs.acs.org/JACS

Anionic Chemistry of Noble Gases: Formation of Mg–NG (NG = Xe, Kr, Ar) Compounds under Pressure

Mao-sheng Miao,^{*,†,‡} Xiao-li Wang,^{§,||} Jakoah Brgoch,[⊥] Frank Spera,^{||} Matthew G. Jackson,^{||} Georg Kresse,[#] and Hai-qing Lin[‡]

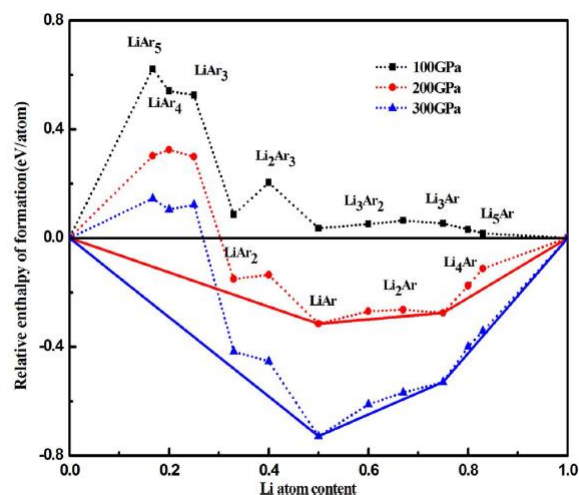
substantially lower pressure is required to stabilize Xe-Mg compounds than Ar/Kr-Mg

SCIENTIFIC REPORTS

OPEN

Stable Lithium Argon compounds under high pressure

Xiaofeng Li^{1,2}, Andreas Hermann³, Feng Peng^{1,2}, Jian Lv¹, Yanchao Wang⁴, Hui Wang⁴ & Yanming Ma^{1,4}



Of course critical pressure is affected by the cation

Nitrogen compounds are not only energetic also superhard!!!

Science 25 August 1989:
Vol. 245 no. 4920 pp. 841-842
DOI: 10.1126/science.245.4920.841

[< Prev](#) | [Table of Contents](#) | [Next >](#)

WEB OF SCIENCE™

REPORTS

Prediction of New Low Compressibility Solids

AMY Y. LIU¹, MARVIN L. COHEN²

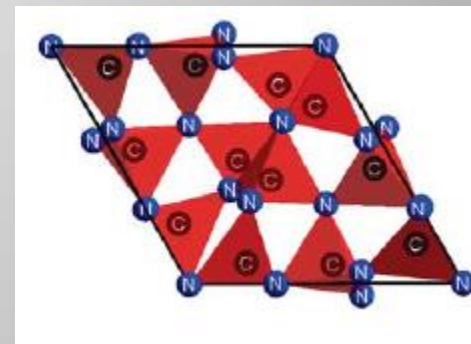
[+ Author Affiliations](#)

Beta carbon nitride (β -C₃N₄/ Si₃N₄)

Web of carbon nitrides

- New class of highly incompressible material, very strong C-N bonds
- C₃N₄ harder than diamond, Holy Grail in the field of superhard materials.

Bulk moduli have been calculated exceeding diamond
Very high densities and wide optical bandgaps (> 3 eV)



Extensive studies aiming at the synthesis of such unique covalent compounds.

- Chemical precursors (e.g. triazine) and mechano-chemical techniques.
- Synthesis of α -, β - and g-C₃N₄ had been reported.
- Identification often ambiguous due to the limited quantity and heterogeneity
- New “C₃N₄” phases have been reported under pressure starting from g-C₃N₄, this could be the result of hydrogen present in starting compounds.

Why 3:4 stoichiometry?

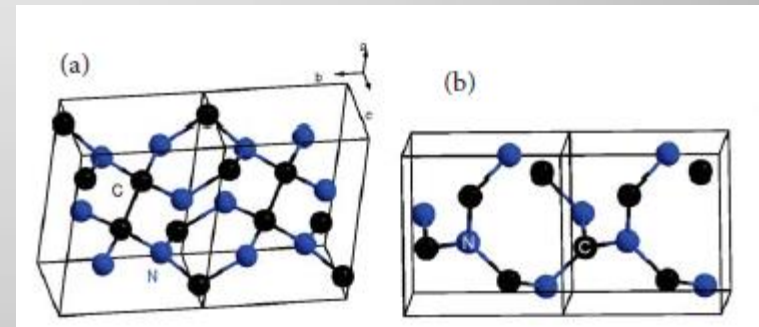
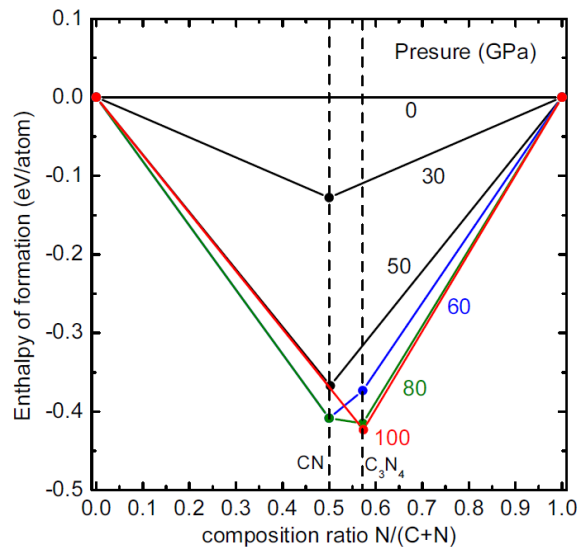
The synthesis of C_3N_4 other than g- C_3N_4 remains elusive.

a priori, the most stable composition for the C-N materials at high pressures is unclear because carbon can exist in both *sp*² and *sp*³ hybridized states.

Cote and Cohen: Carbon nitride compounds with 1:1 stoichiometry (1997).

Initial predictions based on known structural types of AB compounds

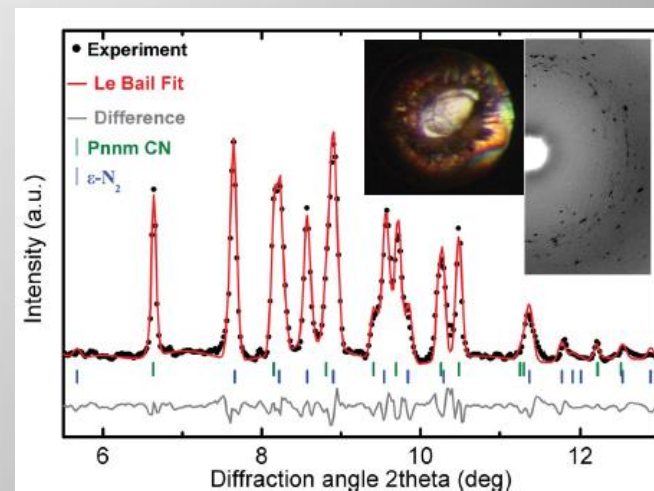
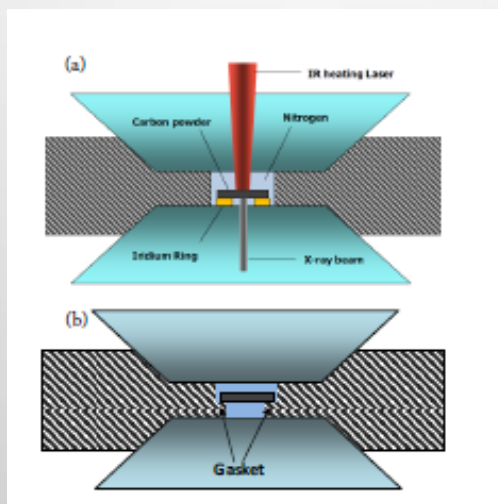
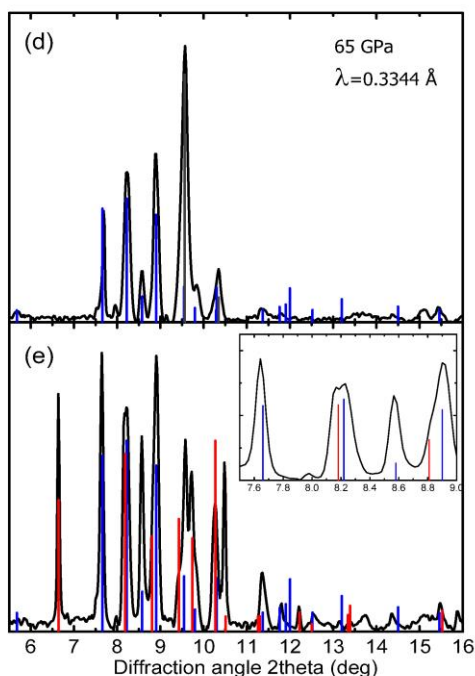
Recent theoretical studies proposed additional structures e.g. cg-CN, *Pnnm* CN



For C-N 1:1 composition, carbon can be either in *sp*² or *sp*³ configurations.

Synthesis of ultra-incompressible sp^3 -hybridized carbon nitride

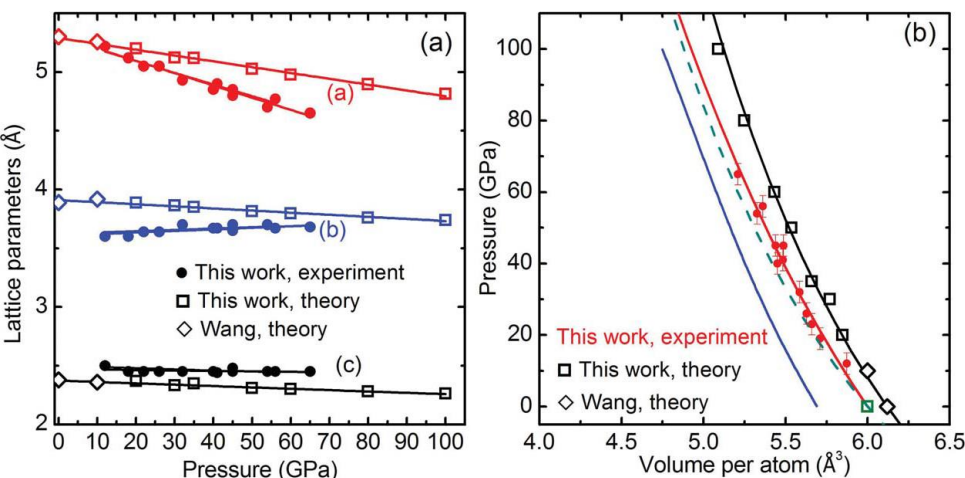
Elemental synthesis by not restricting the initial compositions of the reagents, apply only thermodynamic stimuli.



- Decrease of intensity of N_2 -peaks disappearance of intense HP carbon
- Bragg peaks of the new phase indexed with an orthorhombic *Pnnm* (58)
- Wide band gap material, in favor to the *Pnma* CN phase.

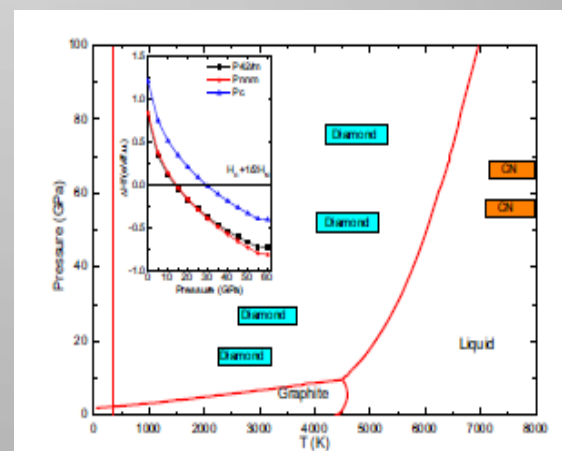
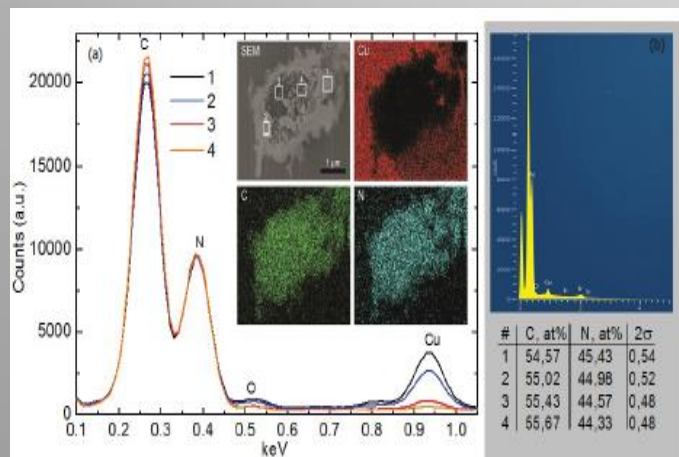
Stavrou *et al.* Submitted

Synthesis of ultra-incompressible sp^3 -hybridized carbon nitride



The compressibility is comparable or even smaller than that of c-BN

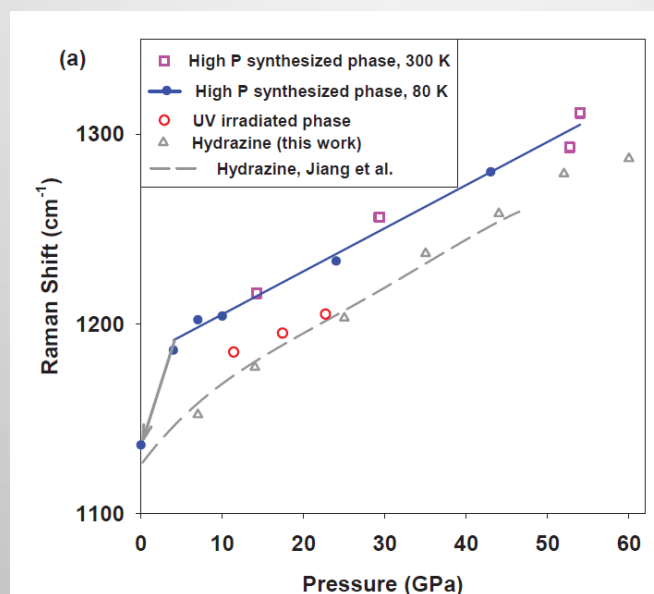
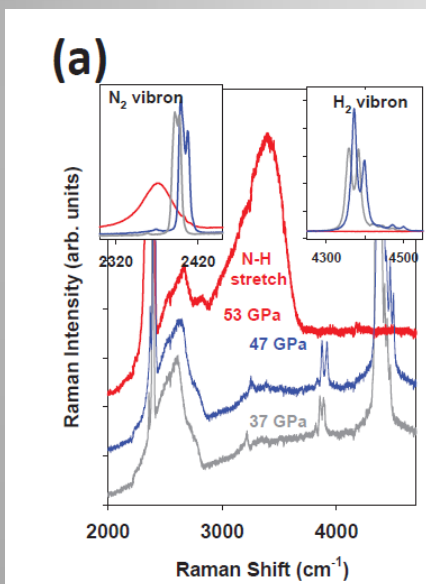
- Below 6 GPa XRD Bragg and Raman peaks disappear.
- EDX: CN compound is preserved and the stoichiometry is close to 1:1.
- $Pnnm$ CN becomes unstable with respect to decomposition.
- Instead of decomposing amorphizes keeping its (metastable) composition.



Backbone NxH Compounds at High Pressures

Formation of oligomeric NxH compounds above 47 GPa under cold compression starting from simple N₂-H₂ mixtures.

These oligomeric compounds can be recovered to ambient pressure at T<130 K,
At room temperature, they can be metastable on pressure release down to 3.5 GPa.



Goncharov et al,
J. Chem. Phys. **142**, 214308 (2015)

Molecular dissociation of N₂ needs >100 GPa and >2000K.
Molecular dissociation of H₂ needs >200 GPa

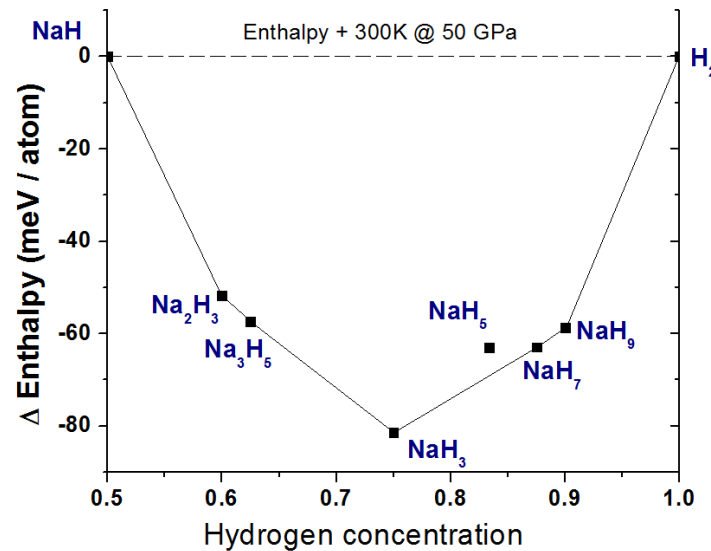
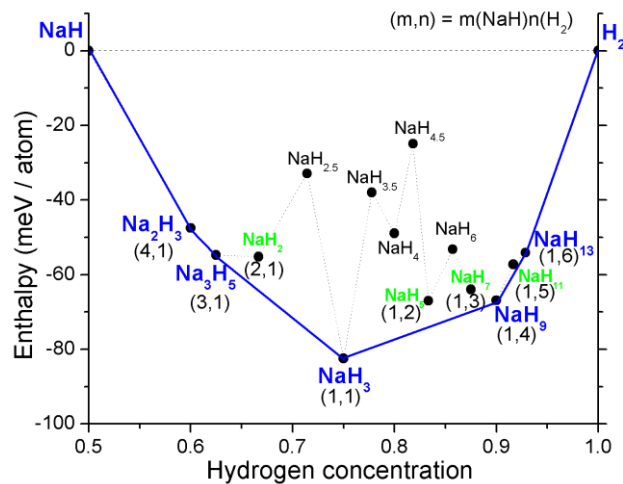
Haber–Bosch process-industrial production of ammonia

This conversion is typically conducted at 15–25 MPa and between 400–500 °C
as the gases are passed over four beds of catalyst, with cooling between each pass

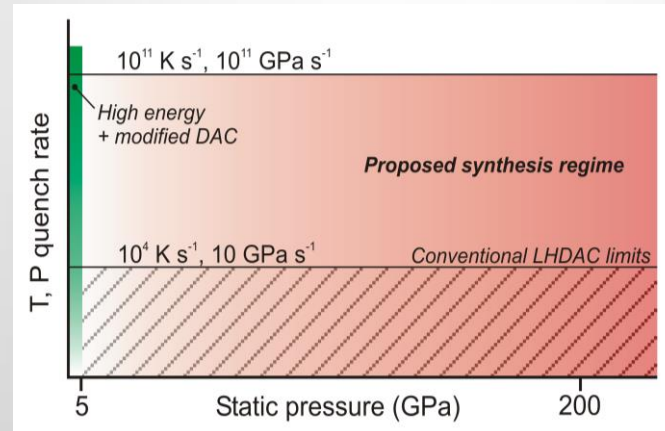
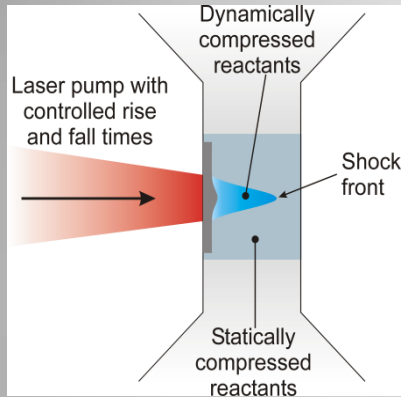
Future studies and challenges

Theory: Shortcomings of existing theoretical predictions for high pressure compounds:

- Exchange approximations
- Based on 0K structural searches (neglect of lattice dynamics)
- Metastable structures are rarely considered



Dynamic compression of precompressed reactants



Dynamically compress, heat, and quench, on an ultrafast time scale, reactants precompressed in conventional diamond anvil cells (DAC).

- Requirements of high static pressure are greatly reduced,
- Synthesized materials are fully encapsulated by the DAC, and
- Ultrafast removal of extreme conditions, quenching of phases and structures.

Acknowledgements

LLNL

J. M. Zaug
J. C. Crowhurst
M. Armstrong
L. Fried
S. Bastea
M. R. Manaa
I-F W. Kuo
Z. Dai
J. R. Jeffries,
R. L. Stillwell
B. Stanimir

CIW

A. Goncharov
V. Struzhkin
S. Lobanov
M. Somayazulu
D-Y Kim
H. Liu

Stony brook Un.

H. Dong
A. Oganov

UCL

Chris J. Pickard

University of South Florida

B. Steele
K. Cong
I. I. Oleynik

Petra III Hamburg

Z. Konopkova
H-P. Liermann

APS Chicago

V. Prakapenka
C. Prescher

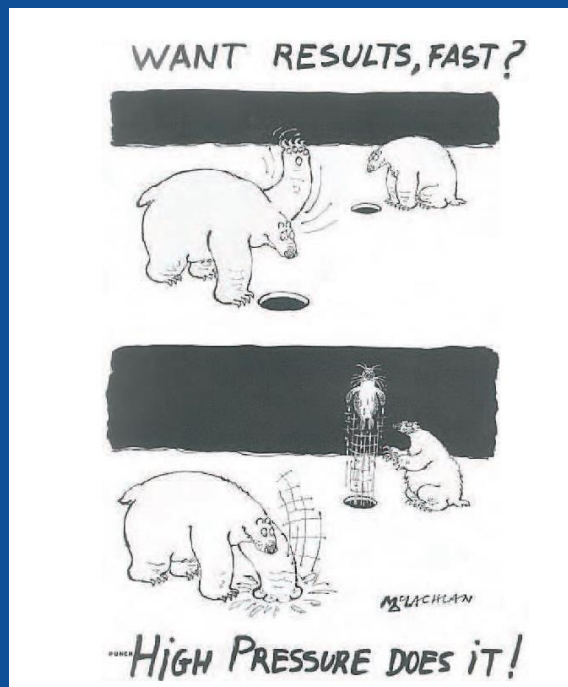
ALS Berkley

B. Kalkan
M. Kunz

Thank you for your attention

Acknowledgments:

This work was performed under the auspices of the U. S. Department of Energy by Lawrence Livermore National Security, LLC under Contract DE-AC52-07NA27344.



Courtesy K. Syassen